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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the diaphragm cover-printing can which consists of a resin coating metal plate for diaphragm cover-printing cans with which it comes to laminate a still more detailed specific resin layer, and this resin coating metal plate about the diaphragm cover-printing can which consists of a resin coating metal plate for diaphragm cover-printing cans, and this resin coating metal plate.

[0002]

[Background of the Invention]The diaphragm cover-printing can (henceforth a DI can) conventionally produced by extracting a steel plate or aluminum plates, such as a tin sheet, and ironing does not have a joint, and is excellent in various physical properties. It is used widely.

[0003]In order to prevent the clever fall by the metal elution from a metal plate, the fall of a flavor, deterioration of contents, generating of a pinhole, etc. in such a DI can, a resin layer may be provided in the can internal side. As a resin coating metal plate which can form the can and such a can in which the resin layer was provided in the such can internal side, the container obtained from the steel plate and this which were covered with the saturated polyester layer is proposed by JP,51-130647,A, for example. The steel plate covered with the polybutylene terephthalate layer is proposed by JP,1-180336,A.

The container obtained from the steel plate and this which were covered with specific saturation copolymerization polyester layers is proposed by JP,1-192545,A, JP,2-57339,A, and JP,3-10835,A.

[0004]By the way, the outstanding moldability which can follow diaphragm ironing is required,

and outstanding adhesion which does not exfoliate from a steel plate is required of the resin for covering used for a diaphragm cover-printing steel-for-can board. Furthermore, the outstanding shock resistance which can bear a canned process and the shock at the time of conveyance is required of this resin at the time of \*\*\*\*. While there is no pinhole leading to corrosion at the time of preservation, the taste of a drink is not affected, i.e., the characteristics, such as excelling in flavor nature, are required.

[0005]However, the resin covered by the conventional steel-for-can board does not necessarily satisfy such a demand. For example, the pinhole might be produced in resin coating at the time of diaphragm ironing. Shock resistance might fall [ the can heated in processes, such as desiccation, printing, and baking, ] after canning.

[0006]

[Objects of the Invention]This invention is made in view of the above conventional technologies, and it excels in a diaphragm cover-printing moldability. It aims at providing the diaphragm cover-printing can which it excels also in shock resistance while excelling in adhesion with a metal plate, and there is no pinhole further, and consists of a resin coating metal plate with which the resin layer which has the characteristics, such as excelling in flavor nature, was laminated, and such a resin coating metal plate.

[0007]

[Summary of Invention]The resin coating metal plate for diaphragm cover-printing cans concerning this invention, Consist of a metal plate and resin coating provided on this metal plate one side, and this resin coating, [A] When it is derived from dicarboxylic acid and a dihydroxy compound and a dicarboxylic acid component is made into 100-mol %, a dicarboxylic acid component, The crystalline saturated polyester resin layer which consists of 99-85 mol of terephthalic acid %, and 1-15 mol of isophthalic acid %, [B] (a) Saturated-polyester resin: 75 to 99 weight section, and (b) Ionomer resin: While consisting of two-layer [ with the resin composition layer which consists of 25 to 1 weight section ], it is characterized by laminating so that the [B] resin composition layer may touch the above-mentioned metal plate.

[0008]The diaphragm cover-printing can concerning this invention is formed from the above resin coating metal plates.

[0009]

[Detailed Description of the Invention]The resin coating metal plate for diaphragm cover-printing cans concerning this invention and the diaphragm cover-printing can which consists of this resin coating metal plate are explained below.

[0010]The resin coating metal plate for diaphragm cover-printing cans concerning this invention consists of a resin composition tunic provided a metal plate and on metal plate one side. In this invention, the conventionally publicly known metal generally used for the can use

is widely used as a metal plate, and a steel plate (tin), a tin-less steel plate (the tin-free steel, electrolysis chromate treatment steel plate), or an aluminum plate etc. by which Sn (tin) plating of the surface was carried out by the publicly known method is used concretely.

[0011] This metal plate is usually 0.1-2 mm in thickness preferably 0.01-5 mm. this metal plate one side or both-sides top -- [A] crystallinity saturated polyester resin layer and [B] (a) Saturated polyester resin and (b) The resin coating which consists of two-layer [ with the resin composition layer which consists of ionomer resin ] is formed.

[0012] [A] crystallinity saturated polyester resin and (a) which are used by this invention Saturated polyester resin is formed from the constitutional unit derived from dicarboxylic acid and a dihydroxy compound.

[0013] Among these, [A] crystallinity saturated polyester resin is copolymerized polyester containing the dicarboxylic acid component derived from two sorts of specific dicarboxylic acid. The dicarboxylic acid component which forms [A] crystallinity saturated polyester resin used by this invention, the time of making a dicarboxylic acid component into 100-mol % -- 99-80 mol of terephthalic acid % -- desirable -- 95-85-mol % and 1-20 mol of isophthalic acid % -- it consists of 5-15-mol % preferably.

[0014] As a dihydroxy ingredient which forms [A] crystallinity saturated polyester resin, Specifically, aliphatic dihydroxy compounds, such as ethylene glycol, a trimethylene glycol (propylene glycol), tetramethylene glycol, pentamethylene glycol, a diethylene glycol, and triethylene glycol, are mentioned.

[0015] The above [A] crystallinity saturated polyester, The constitutional unit derived in the range which does not spoil the purpose of an invention from multifunctional compounds, such as trimesic acid, pyromellitic acid, trimethylolethane, trimethylolpropane, trimethylolmethane, and pentaerythritol, may be included in the quantity not more than 2 mol % in small quantities.

[0016] [A] crystallinity saturated polyester used by this invention is a parenchyma top line. This is checked when this saturated polyester dissolves in o-chlorophenol.

[0017] It is usually preferably preferred [ [A] crystallinity saturated polyester used by this invention ] 0.5 to 1.0 dl/g respectively that it is 0.6 - 1.0 dl/g still more preferably for the limiting viscosity [eta] measured at 25 °C in o-chlorophenol 0.5 to 1.4 dl/g.

[0018] The saturated polyester which has such limiting viscosity [eta] is excellent also in mechanical strengths, such as shock resistance, and preferred while it is excellent in melt molding nature and a diaphragm cover-printing moldability.

[0019] 50-120 °C of glass transition temperature (T<sub>g</sub>) of [A] crystallinity saturated polyester resin used by this invention is usually 60-100 °C preferably.

It is desirable for 130-210 °C of low-temperature crystallization temperature (T<sub>c</sub>) to be usually 140-200 °C preferably, and for 210-265 °C of crystal melting points (T<sub>m</sub>) to be usually 220-260

\*\* preferably.

[0020]As for [A] crystallinity saturated polyester resin used by this invention, it is desirable for the degree of crystallinity measured by an X-ray diffraction method to be 10 to 60% preferably 5 to 75%.

[0021][A] crystallinity saturated polyester resin used by this invention which has the above presentations, While excelling in processability, compared with the tunic formed from the conventionally publicly known polyester resin derived from terephthalic acid and ethylene glycol, the tunic formed from this [A] crystallinity saturated polyester resin cannot adsorb a terpene series bad smell easily, and is excellent in the smell retaining property.

[0022](a) used in this invention when forming the [B] resin composition layer Saturated polyester resin, a dicarboxylic acid component -- terephthalic acid or its ester derivative (for example, lower alkyl ester.) It consists of phenyl ester etc. and a dihydroxy ingredient consists of ethylene glycol or its ester plasticity derivatives (for example, monocarboxylic acid ester ethyleneoxide etc.).

[0023]This (a) Saturated polyester may contain the constitutional unit derived from other dicarboxylic acid and/or other dihydroxy compounds in the quantity not more than 40 mol %. As dicarboxylic acid other than terephthalic acid, concretely Phthalic acid, isophthalic acid, Aromatic dicarboxylic acid, such as naphthalene dicarboxylic acid, diphenyldicarboxylic acid, and difenoxycarboxylic acid; Adipic acid, Aliphatic dicarboxylic acid, such as sebacic acid, azelaic acid, and decane dicarboxylic acid; alicycle fellows dicarboxylic acid, such as cyclohexanedicarboxylic acid, etc. are mentioned.

[0024]Dicarboxylic acid other than these terephthalic acid may be used as the ester derivative. As dihydroxy compounds other than ethylene glycol, Specifically Propylene glycol, tetramethylene glycol, neopentyl glycol, Hexamethylene glycol, dodecamethyleneglycol, a diethylene glycol, Alicycle fellows glycols, such as aliphatic series glycol; cyclohexane dimethanol, such as triethylene glycol, tetraethylene glycol, and a polyethylene glycol; Bisphenols. Aromaticdiol, such as hydroquinone and 2,2-bis(4-beta-hydroxyethoxyphenyl) propane, is mentioned.

[0025]These dihydroxy compounds may be used as the ester derivative. (a) saturated polyester used by this invention, The constitutional unit derived from multifunctional compounds, such as trimesic acid, pyromellitic acid, trimethylolethane, trimethylolpropane, trimethylolmethane, and pentaerythritol, may be included in the quantity not more than 2 mol % in small quantities.

[0026]Such (a) Saturated polyester is a parenchyma top line.

This is checked when this saturated polyester dissolves in o-chlorophenol.

As for the limiting viscosity  $[\eta]$  which measured the saturated polyester used by this invention

at 25 \*\* in o-chlorophenol, it is usually preferably desirable that it is 0.6 - 1.0 dl/g still more preferably 0.5 to 1.0 dl/g 0.5 to 1.4 dl/g.

[0027](a) which has such limiting viscosity [eta] Saturated polyester is excellent also in mechanical strengths, such as shock resistance, and preferred while it is excellent in melt molding nature and a diaphragm cover-printing moldability.

[0028](a) used by this invention As for saturated polyester resin, it is desirable for 50-120 \*\* of glass transition temperature (Tg) to be usually 60-100 \*\* preferably. This (a) When saturated polyester resin may be amorphism nature, or may be crystallinity and it is crystallinity, 210-265 \*\* of crystal melting points (Tm) are usually 220-260 \*\* preferably.

It is desirable for 130-210 \*\* of low-temperature crystallization temperature (Tc) to be usually 135-205 \*\* preferably.

[0029]At this invention, it is (a). Although not limited in particular as saturated polyester resin, it is preferred to use amorphism nature or saturated polyester resin which is amorphism nature mostly in that an adhesive property with metal is excellent also among the above, and it excels in shock resistance.

[0030](b) used in this invention when forming the [B] resin composition layer Although publicly known ionomer resin is conventionally used widely as ionomer resin, This ionomer resin is the ionic salt in which a part or all of the carboxyl group in the copolymer of ethylene and alpha and beta-unsaturated carboxylic acid was neutralized with the metallic cation.

[0031]As this alpha and beta-unsaturated carboxylic acid, acrylic acid, methacrylic acid, maleic acid, itaconic acid, a maleic anhydride, maleic acid monomethyl ester, maleic acid monomethyl ester, etc. are mentioned to the unsaturated carboxylic acid of the carbon numbers 3-8, and a concrete target.

[0032]As a metallic cation which neutralizes the carboxyl group in the copolymer of such ethylene and unsaturated carboxylic acid, Concretely, 1 - divalent metallic cations, such as Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Zn<sup>++</sup>, Mg<sup>++</sup>, Ca<sup>++</sup>, Co<sup>++</sup>, nickel<sup>++</sup>, Mn<sup>++</sup>, Pb<sup>++</sup>, and Cu<sup>++</sup>, are mentioned. A part of carboxyl group of the emainder which is not neutralized with a metallic cation may be esterified with lower alcohol.

[0033](b) used by this invention Although ionomer resin is metal salt of the copolymer of ethylene and unsaturated carboxylic acid as mentioned above, the constitutional unit to which the copolymer with the ethylene and unsaturated carboxylic acid for forming metal salt is derived from ethylene -- 80-99-mol % -- it is 85-98-mol % preferably.

the constitutional unit (constitutional unit which has a carboxyl group) derived from unsaturated carboxylic acid -- 1-20-mol % -- it contains in% of the amount of 2-15 mol preferably.

[0034](b) used by this invention In ionomer resin, 15 to 100% of carboxyl group is specifically

neutralized for a part or all of the carboxyl group in the copolymer of ethylene and unsaturated carboxylic acid. This degree of neutralization is 30 to 70% still more preferably 20 to 80% preferably.

(b) of such a degree of neutralization The constituent formed from ionomer resin is excellent in melting extrusion nature.

[0035]Such (b) As ionomer resin, Specifically A copolymer, or ethylene and maleic acid with unsaturation monocarboxylic acid, such as ethylene, acrylic acid, and methacrylic acid, The ionomer resin in which a part or all of the carboxyl group in a copolymer with unsaturated dicarboxylic acid, such as itaconic acid, was neutralized with metal ions, such as sodium, potassium, lithium, zinc, magnesium, and calcium, is mentioned.

[0036]That by which 30 to 70% of the carboxyl groups in the copolymer (the constitutional unit which has a carboxyl group is 2-15-mol %) of ethylene, acrylic acid, or methacrylic acid were neutralized with metal, such as Na and Zn, is [ among these ] preferred.

[0037]What was neutralized with metal, such as Na and Zn, and the thing which is not neutralized can also be blended and used.

[0038]As these ionomer resin, commercial items, such as "high milan" (trade name: made in Mitsui E. I. du Pont de Nemours Pori Kem Cal), can be used. In this invention, the [B] resin composition is (a). Saturated polyester resin and (b) When the sum total with ionomer resin is made into 100 weight sections, The above (a) It is the quantity of 80 to 95 weight section preferably 75 to 99 weight section about saturated polyester resin, and is (b). Ionomer resin is preferably contained in the quantity of 18 to 7 weight section still more preferably 20 to 5 weight section one to 25 weight section.

[0039]Such a [B] resin composition is 27 or less J/g in cold crystallization heat quantity.

And it is desirable for the amount of heat of fusion to be 30 or less J/g.

Cold crystallization heat quantity (J/g) is the calorific value by crystallization observed when it measures with 10 °C the heating rate for /using a differential thermal analyzer (Perkin Elmer-7 type).

[0040]Can prepare the above [B] resin compositions with the preparing method of a publicly known resin composition conventionally, and specifically, (a) Saturated polyester resin and (b) Ionomer resin can be prepared by carrying out melting mixing with an extrusion machine, a kneader Banbury mixer, etc. further, after mixing with a tumbler blender, a Henschel mixer, a V type blender, etc.

[0041]In this invention, the resin coating laminated on a metal plate is laminated so that the [B] resin composition layer may touch the above-mentioned metal plate, while consisting of two-layer [ of the above [A] crystallinity saturated polyester resin layers and the [B] resin composition layer ].

[0042]The thickness of the resin layer laminated in this way is the two-layer sum total, and is 5-500 micrometers usually 20-60 micrometers especially preferably 10-100 micrometers preferably. As for the two-layer film parameter of these [A] crystallinity saturated polyester resin layer and the [B] resin composition layer, it is preferred that it is [A] layer:[B] layer =2:1-1:9.

[0043][A] When the layer/[B] layer is over 2, it may be inferior to shock-resistant intensity. A pinhole may occur with the can obtained by on the other hand it being sometimes difficult to laminate continuously that the [A] layer / [B] layer is less than 1/9 by uniform thickness to up to a metal plate.

[0044]The resin coating metal plate concerning above this inventions is manufactured as follows, for example.

(1) [A] crystallinity saturated polyester resin and the [B] resin composition prepared as mentioned above are simultaneously extruded so that the [B] resin layer may touch a metal plate on a metal plate by a two-layer extrusion T die.

[0045](2) Form the film which once consists of a [A] crystallinity saturated polyester resin layer and a [B] resin composition layer, and paste this film and metal plate together so that the [B] resin composition layer may touch a metal plate.

[0046](3) The [B] resin composition layer can be formed on a metal plate, and, subsequently to this [B] resin composition layer top, [A] crystallinity saturated polyester resin layer can also be formed. As for the resin coating which faced covering a resin layer on a metal plate as mentioned above, was extruded by the molten state from the extrusion machine, and was covered on the metal plate, quenching is preferred.

[0047]Thus, as for the resin coating provided on the metal plate, it is preferred that it is for undivided substantially and is amorphous state. It may face forming the above resin coatings on a metal plate, and additive agents, such as weathering stabilizer, lubricant, a thermostabilizer, and a shock-resistant improving agent, may be made to contain in each resin layer if needed, and further, after these additive agents form the masterbatch which consists of each resin and an additive agent beforehand, they may be added.

[0048]The method of of (1) simultaneously extruded by a two-layer extrusion T die among these is preferred in order to tend to form the diaphragm cover-printing can excellent in quality without a pinhole from the resin coating metal plate obtained by this method, while excelling in a manufacturing-cost side. Although the resin coating metal plate with which the method of of (2) pasted together once it uses a film is obtained while a manufacturing cost increases compared with the method of (1) is inferior to the result of a pinhole test, there are things. The film of a uniform two-layer structure of having a specific film parameter may not be obtained, the method of (3) may be inferior to the adhesion between the [A] layer and the [B] layer, or a foreign matter (garbage) etc. may mix it.

[0049]The resin coating metal plate concerning this invention as mentioned above a metal plate and on this one side, [A] It consists of a tunic which a crystalline saturated polyester resin layer and the [B] resin composition layers are the above film parameters, and was laminated so that the [B] resin composition layer might touch a metal plate, Uniform processing is carried out without excelling in a moldability, especially a diaphragm cover-printing moldability, and producing a pinhole in a tunic at the time of shaping, while having the outstanding shock resistance. Since this resin coating is excellent also in adhesion with a metal plate and it excels in the processing flattery nature at the time of shaping, the can excellent in appearance is obtained.

[0050]The resin coating metal plate concerning this invention can reveal the characteristics, such as diaphragm ironing nature outstanding by being formed by a resin layer specific as mentioned above.

[0051]When the [A] layer is formed with gay polyethylene terephthalate, a blister may be generated after canning. When the [A] layer is formed by the copolymerized polyester which contains an isophthalic acid component at 20-mol %, the punch omission at the time of canning may become it is bad and difficult [ it / to manufacture a can continuously ], and the can moreover obtained may be inferior to evaluation of a pinhole test, flavor adsorption property, etc.

[0052]If (b) ionomer resin is used in the quantity exceeding 25 weight sections when preparing the resin composition which forms the [B] layer, (b) ionomer resin and (a) polyester resin will become that it is hard to be mixed uniformly. For this reason, the resin composition which contains (b) ionomer resin in the quantity exceeding 25 weight sections cannot form the resin layer of fixed thickness for a resin layer easily on a metal plate by generating BUTSU and gel, and may produce a pinhole at the time of diaphragm ironing. The diaphragm cover-printing can furthermore obtained also has problems, like flavor adsorption is large. When the [B] layer is formed without on the other hand using (b) ionomer resin, it may be inferior to impact strength and may become weak.

[0053]Replace with the still more above resin coatings and the [A] layer For example, polyethylene terephthalate or polybutylene terephthalate; 75 - 100 weight section 90 - whose 100-mol% of dicarboxylic acid components are terephthalic acid, Ionomer; Polyethylene terephthalate; 1 whose 75-100 mol of a dicarboxylic acid component it is formed with the constituent which consists of zero to 25 weight section, and the [B] layer is terephthalic acid - 40 weight section, Polybutylene terephthalate whose 60-100-mol% of dicarboxylic acid components are terephthalic acid; 30 to 85 weight section, Ionomer; if the metal plate formed with the constituent which consists of ten to 30 weight section is extracted and ironed, the can it is not only difficult to be easy to produce a pinhole and to obtain a practical can, but obtained is difficult for flavor adsorption to obtain the suitable, very large diaphragm cover-printing can



for a soft drink use.

[0054]When manufacturing a diaphragm cover-printing can, polyethylene terephthalate, The copolymerized polyester which contains terephthalic acid and isophthalic acid as a dicarboxylic acid component, If the metal plate which covered the constituent which consists of ionomers is used, it is difficult to be easy to produce a pinhole at the time of diaphragm ironing, and for thickness and crystalline variation to become large, and to obtain a diaphragm cover-printing can stably.

[0055]The above resin coating metal plates extract the diaphragm cover-printing can concerning this invention, and it comes to carry out ironing. Under the present circumstances, when the resin coating metal plate with which resin coating was provided only in one side of the metal plate is used, ironing is extracted and carried out so that a resin coating side may be on a can internal side.

[0056]Since the diaphragm cover-printing can by which not only can internal but the can outside surface was covered by resin will be obtained if resin coating uses the resin coating metal plate formed in both sides when extracting from the above-mentioned resin coating metal plate and manufacturing a cover-printing can, Usually, the painting process of the can outside surface performed after canning can be skipped, and canning equipment is also substantially reducible while there is also no problem at the time of paint of a solvent dispersing.

[0057]Various kinds of publicly known methods can be used for the method of manufacturing a diaphragm cover-printing can (DI can). It can manufacture by the single step or the method of ironing several steps, using cover-printing punch as most general method.

[0058]For example, diaphragm ironing can be performed under the following conditions. Diameter of a plank -- 100-200-mm diaphragm conditions -- One-step contraction ratio 1.1-2.42-step contraction ratio Diameter of 1.1 - 1.6 diaphragm cover printing -- Three-step ironing The 20-100 mmphi total ironing rate -- the diaphragm cover-printing can which takes 20 to 80% for this invention, On the metal plate, the two-layer tunic of [A] crystallinity saturated polyester resin layer and the [B] resin composition layer is formed so that [A] crystallinity saturated polyester resin layer may touch the contents of a can.

While there is little especially adsorption of a terpene series bad smell and it is excellent in flavor nature (smell retaining property), there is no pinhole into a tunic and it excels in the mothball nature of contents.

[0059]

[Effect of the Invention]The resin coating metal plate for diaphragm cover-printing cans concerning this invention is excellent in the adhesion of resin and a metal plate. It excels in a diaphragm cover-printing moldability, and excels in the imitation nature of resin at

the time of a fabricating operation, and a fish eye can form the diaphragm cover-printing can which was excellent in appearance few.

[0060]The diaphragm cover-printing can concerning this invention has the outstanding shock resistance which can bear \*\*\*\*, a canned process, and the shock at the time of conveyance. After canning, even if heated in processes, such as desiccation, printing, and baking, the outstanding shock resistance is held.

[0061]The diaphragm cover-printing can concerning this invention does not have a pinhole, and while excelling in the mothball nature of contents, it excels also in preservability, such as a scent of contents, and flavor nature (smell retaining property).

[0062]

[Example]Next, this invention is not limited by these examples although an example explains this invention concretely.

[0063]

[Examples 1-8] [A] crystallinity saturated polyester resin shown in Table 1, and [B (a)] ionomer resin which has a presentation as shown in Table 1 Saturated polyester resin and (b) (high milan 1706:Mitsui E. I. du Pont de Nemours & Co..) Trade name; the steel plate in which the resin composition which becomes except for Example 8 was given to Sn plating of  $2.8 \text{ g/m}^2$  per one side to both sides (board 0.245 mm in thickness.) On Sn plating layer with a hardness of T-4 about of one side, the two-sort two-layer extrusion T die was used, and as the [B] layer touched the steel plate by the film parameter shown in Table 1, it covered with 30-micrometer sum total thickness. The steel plate by which resin was covered by the T die was quenched to 100 \*\* or less within 10 seconds using what heated the steel plate at the time of covering.

[0064]Table 1 -- the intrinsic viscosity [dl/g] of [A] crystallinity saturated polyester resin, and (a) Tg (glass transition temperature) of each saturated polyester resin, Tm (melting point), and Tc (low-temperature crystallization temperature) are shown.

[0065]Tg, Tm, and Tc were measured with the heating rate by a part for 10 \*\*/using the differential thermal analyzer (Perkin Elmer-7 type). Tg seen at the time of temperature up considered it as the temperature of the intersection of the tangent of a peak, and Tc and Tm were taken as the temperature of the peak of a peak.

[0066]Thus, as the resin coating side turned into can internal, extracted the resin coated steel of the acquired ordinary temperature in the following process condition, and it extracted by performing ironing, and the cover-printing can was manufactured.

[0067]resin temperature [ in front of <process condition> 1. diaphragm ironing ]: -- diameter of ordinary temperature 2. plank: -- 137-mm3. diaphragm condition: -- one-step contraction ratio 1.62-step contraction ratio 1.34. cover-printing punch diameter: -- 65.8 mm of three-step

ironing phi5. total ironing-rate: -- 67% [0068](i) The inner surface of the can was washed after the adhesion evaluation diaphragm ironing of can internal coated resin, and 210 \*\* observed and estimated the grade of peeling of resin of the tip part of the can after 10-minute preburn in oven. A valuation basis is shown in Table 2.

[0069](ii) wash the inner surface of a can after blister evaluation diaphragm ironing, and attach a can -- 210 \*\* observed and estimated in oven the blister (bulging) formed in the pars basilaris ossis occipitalis of the can after 10-minute preburn at \*\*\*\*\*. A valuation basis is shown in Table 2.

[0070](iii) The diaphragm cover-printing can after paint of the shock-proof evaluation can outside surface of resin coating and baking was filled up with 1.0% of salt solution, and it retorted at 120 \*\* for 30 minutes. It fell from the pars basilaris ossis occipitalis from a height of 30 cm to the griddle of the angle of 45 degrees after cooling to the room temperature after processing. The salt solution after fall and inside a can was thrown away, the salt solution which a few exceeded near the shock part was used as the negative pole, and the current of 6V was sent by using the outer wall of a can as the anode. The current value (mA) which flows at this time was measured. A valuation basis is shown in Table 2.

[0071](iv) 1.0% of salt solution was filled up with 210 \*\* into the can after 10-minute preburn in oven after pinhole evaluation of can internal coated resin, or preece test pinhole evaluation diaphragm ironing, the outer wall of the can was used as the anode for the salt solution at the negative pole, and the current of 6V was sent. The current value (mA) which flows at this time was measured. A valuation basis is shown in Table 2.

[0072]Depositing copper was observed, after having put the chemical-plating liquid of copper containing 20g/l. of sulfuric acid, and 50g/l. of copper sulfate ( $\text{CuSO}_4$  and  $7\text{H}_2\text{O}$ ) in preece test profitable \*\*\*\*\* , neglecting it for 10 minutes and removing and rinsing liquid. If the resin layer of can internal has lack (pinhole), iron will be eluted from a lack part and substitution plating of the copper will be carried out.

[0073](V) The inner surface of the can which is the evaluation above of flavor adsorption property and was produced by making was washed, and it dried in about 2 minutes using 210 \*\* oven. It burned by furthermore painting a can outside surface. In this way, the obtained can was filled up with the 5% ethanol solution containing 20 ppm limonene, and it was neglected for 20 \*\* and ten days. The can obtained by the following comparative examples 1 in the amount of adsorption to the film of limonene was compared as 100 (when gay PET is used for an inner surface).

[0074]

[Comparative example 1] The resin coating metal plate was obtained like the example except having formed the tunic (monolayer) which consists of crystalline saturated polyester resin as shown in Table 1 by a thickness of 30 micrometers.

[0075]Canning of this resin coating metal plate was carried out like the example. About the obtained can, test evaluation was carried out like the example. A result is shown in Table 3.

[0076]The intrinsic viscosity [dl/g] of this crystalline saturated polyester resin, Tg, Tm, and Tc are shown in Table 1.

[0077]

[Comparative example 2] The resin coating metal plate was obtained like the example except having formed the tunic (monolayer) which consists of saturated polyester resin as shown in Table 1 by a thickness of 30 micrometers.

[0078]Canning of this resin coating metal plate was carried out like the example. About the obtained can, test evaluation was carried out like the example. A result is shown in Table 3.

[0079]The intrinsic viscosity [dl/g] of this crystalline saturated polyester resin, Tg, Tm, and Tc are shown in Table 1.

[0080]

[Table 1]

表 1

	層	各層の飽和ポリエステル樹脂					[B] 7477- 樹脂 <sup>2</sup> 重量部	膜厚比 [A] — [B]
		組 成	固有粘度 [dl/g]	DSC				
				T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)		
実施例 1	[A]	4777 <sup>1</sup> 酸 <sup>1</sup> 54%	1. 1	7 1	15 2	2 3 8		1
	[B]	4777 <sup>1</sup> 酸 <sup>1</sup> 16%	0. 8 5	7 3	15 6	2 2 9	1 7	2
実施例 2	[A]	4777 <sup>1</sup> 酸 54%	1. 1	7 1	15 2	2 3 8		1
	[B]	4777 <sup>1</sup> 酸 7. 7%	0. 6 8	7 2	15 5	2 3 2	1 5	3
実施例 3	[A]	4777 <sup>1</sup> 酸 54%	1. 1	7 1	15 2	2 3 8		1
	[B]	4777 <sup>1</sup> 酸 6. 9%	0. 8 5	7 2	15 4	2 3 4	1 7	2
実施例 4	[A]	4777 <sup>1</sup> 酸 10%	1. 1	7 2	16 7	2 2 3		1
	[B]	4777 <sup>1</sup> 酸 10%	0. 8 5	7 3	15 6	2 2 9	1 7	2
実施例 5	[A]	4777 <sup>1</sup> 酸 10%	1. 1	7 2	16 7	2 2 3		1
	[B]	4777 <sup>1</sup> 酸 7. 7%	0. 6 8	7 2	15 5	2 3 2	1 5	3
実施例 6	[A]	4777 <sup>1</sup> 酸 10%	1. 1	7 2	16 7	2 2 3		1
	[B]	4777 <sup>1</sup> 酸 6. 9%	0. 8 5	7 2	15 4	2 3 4	1 7	2
実施例 7	[A]	4777 <sup>1</sup> 酸 10%	1. 1	7 2	16 7	2 2 3		1
	[B]	CHDM <sup>3</sup> 30%	0. 8 5	7 6	—	—	1 2	2
実施例 8	[A]	4777 <sup>1</sup> 酸 10%	1. 1	7 2	16 7	2 2 3		1
	[B]	4777 <sup>1</sup> 酸 10%	0. 8 5	7 3	15 5	2 2 9	1 5 <sup>4</sup>	2
比較例 1	ホモPET <sup>4</sup>		1. 5	7 3	16 9	2 5 2		
比較例 2	CHDM 54%		1. 1	7 3	17 4	2 4 0		

[0081]\* 1[A] copolymerized polyester resin : make a dicarboxylic acid component into 100-mol %. Dicarboxylic acid components other than isophthalic acid are terephthalic acid.

\* 2 (a) Copolymerized polyester resin; a dicarboxylic acid component is made into 100-mol %. [0082]Dicarboxylic acid components other than isophthalic acid are terephthalic acid.

\* 3 (a) Copolymerized polyester resin; a dihydroxy ingredient is made into 100-mol %.

[0083]Dihydroxy ingredients other than CHDM (cyclohexane dimethanol) are ethylene glycol.

[0084]\*4) Gay PET : crystalline polyester made of Mitsui Pet resin.

\* 5 [B] resin compositions : the sum totals of ionomer resin and saturated polyester resin are 100 weight sections.

[0085]\*6) Ionomer : high milan 1707 (Mitsui and made in E. I. du Pont de Nemours Pori Kem Cal, trade name)

[0086]

[Table 2]

表 2

評 価	(i) 密着性試験	(ii) プリスター	(iii) 衝撃試験 (mA)	(iv) 引っ張り試験 (mA)
◎	剥離なし	プリスターなし。	0	0
○	0.5mm 以下の剥離がある。	直径2mm 以下の剥離が希にある。	0.01~0.03	0.0~0.5
△	0.5 ~1.0mm 剥離が部分的にある。	直径2mm 以下の剥離が多少全数にある。	0.03~0.10	0.5 ~1.0
×	0.5 ~1.0mm 剥離がある。	全径に直径5mm 以下の剥離がある。	0.10~1.00	1.0 ~2.0
××	2.0mm 以上の剥離がある。	全径に直径10mm 以下の剥離がある。	1.0 ~10.0	2.0 ~5.0
×××	全径に剥離がある。	非常に大きい剥離が全径にある。	10.0以上	5.0 以上

[0087]

[Table 3]

表 3

	密着性	ブリスター	衝撃試験	ビード試験	70-60 取替
実施例 1	◎	◎	◎	○	6.2
実施例 2	◎	◎	◎	○	5.8
実施例 3	○	◎	◎	○	5.7
実施例 4	◎	◎	◎	○	3.7
実施例 5	◎	◎	◎	○	3.8
実施例 6	○	◎	◎	○	3.6
実施例 7	◎	△	◎	○	3.7
実施例 8	◎	◎	◎	○	3.9
比較例 1	××	×	×	×	10.0
比較例 2	××	△	×	×	11.6

[0088]

[Comparative examples 3-6] The resin coating metal plate was obtained like the example except having formed the tunic which consists of saturated polyester resin as shown in Table 4 by a thickness of 30 micrometers. Canning of this resin coating metal plate was carried out like the example. The result which carried out test evaluation like the example about the obtained can is shown in Table 5.

[0089]

[Comparative example 7] Biaxial extension of the polyethylene terephthalate (PET) (IV=0.69) as shown in Table 4 was carried out one by one with the conventional method melt extruding, 3.5 times as many length, and horizontally [ 3.7 times as many ], stress heat setting was carried out at 235 \*\*, and the 16-micrometer-thick PET-BO (biaxial extension PET) film was created. The extrusion lamination of the [B] layer shown in Table 4 on the obtained PET-BO tunic was carried out to a thickness of 14 micrometers, and the two-layer film was created. On the same steel plate as an example, it pasted up and water-cooled with the steel plate temperature of 220 \*\*, and the resin coating metal plate was created so that the [B] layer might touch a steel plate. Canning of this resin coating metal plate was carried out like the example. The result which carried out test evaluation like the example about the obtained can is shown in Table 5.

[0090]

[Table 4]

表 4

	各層の飽和ポリエステル樹脂			7イマ- 樹脂**1	膜厚比
	組 成		固有粘度		
				[dl／g]	重量部
比較例 3	[A]	C o - P E T **2 (TA/IA=90/10)	1 . 1		1
	[B]	新エチレンテレフタレート 3 5 重量部 C o - P B T **3 5 0 重量部 (TA/IA=70/30)	0 . 9 2	1 5	2
比較例 4	[A]	C o - P E T (TA/IA=90/10)	1 . 1		1
	[B]	C o - P E T 5 0 重量部 (TA/IA=70/30) 新ブチレンテレフタレート 3 5 重量部	0 . 9 3	1 5	2
比較例 5	[A]	ポリブチレンテレフタレート	1 . 6		1
	[B]	C o - P E T (TA/IA=90/10)	0 . 8 5	1 7	2
比較例 6	[A]	C o - P E T (TA/IA=90/10)	1 . 1		1
	[B]	C o - P E T (TA/IA=90/10)	0 . 8 5	3 0	2
比較例 7	[A]	P E T - B O フィルム**4	0 . 6 9		1
	[B]	C o - P E T (TA/IA=90/10)	0 . 8 5	1 7	1

\* 1) [B] 樹脂組成物；アイオノマー樹脂とポリエステル樹脂との合計が  
100重量部である。

\* 2) Co-PET；ジカルボン酸成分がテレフタル酸（TA）／イソフタル酸  
（IA）（モル比）とからなり、  
ジヒドロキシ成分がエチレングリコールである共重合ポリエステル

\* 3) Co-PBT；ジカルボン酸成分がテレフタル酸（TA）／イソフタル酸  
（IA）（モル比）とからなり、  
ジヒドロキシ成分が1,4-ブタンジオールである共重合ポリエステル

\* 4) PET-BO；2軸延伸ポリエチレンテレフタレート

[0091]

[Table 5]



表 5

	(i) 密着性評価	(ii) 耐溶剤性評価	(iii) 耐衝撃試験	(iv) ビッカース試験	(v) フレック 吸着
比較例 3	×	×	×	×	9.5
比較例 4	×	×	×	×	9.8
比較例 5	△	×	×	×	*
比較例 6	×	△	×	×	4.0
比較例 7	×	×	×	×	12.0

\*吸着量が他のものと比べて大変多い。

[0092]

[Examples 9-16] The resin coating metal plate was obtained like Example 1 except having formed the tunic which consists of saturated polyester resin as shown in Table 6 by a thickness of 30 micrometers. Canning of this resin coating metal plate was carried out like Example 1. The result which carried out test evaluation like Example 1 about the obtained can is shown in Table 8.

[0093]

[Comparative examples 8-14] The resin coating metal plate was obtained like Example 1 except having formed the tunic which consists of saturated polyester resin as shown in Table 7 by a thickness of 30 micrometers. Canning of this resin coating metal plate was carried out like Example 1. The result which carried out test evaluation like Example 1 about the obtained can is shown in Table 8.

[0094]

[Table 6]

表 6

	層	各層の成分(ポリエステル樹脂)						[B] 7477- 樹脂 <sup>5</sup> 重量部	膜厚比 [A] — [B]
		組 成	固有粘度 [dl/g]	DSC					
				T <sub>g</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)			
実施例9	[A]	477% 酸 2% 酸	1. 1	7 1	1 4 8	2 4 5		1	
	[B]	477% 酸 10% 酸	0. 8 5	7 3	1 5 5	2 2 9	1 5	2	
実施例10	[A]	477% 酸 15% 酸	1. 1	7 2	1 5 5	2 3 0		1	
	[B]	477% 酸 10% 酸	0. 8 5	7 3	1 5 5	2 2 9	1 5	2	
実施例11	[A]	477% 酸 10% 酸	1. 1	7 2	1 6 7	2 2 3		1	
	[B]	477% 酸 10% 酸	0. 8 5	7 3	1 5 5	2 2 9	2 5	2	
実施例12	[A]	477% 酸 10% 酸	1. 1	7 2	1 6 7	2 2 3		2	
	[B]	477% 酸 10% 酸	0. 8 5	7 3	1 5 5	2 2 9	1 5	1	
実施例13	[A]	477% 酸 10% 酸	1. 1	7 2	1 6 7	2 2 3		1	
	[B]	477% 酸 10% 酸	0. 8 5	7 3	1 5 5	2 2 9	1 5	9	
実施例14	[A]	477% 酸 2% 酸	1. 1	7 1	1 4 8	2 4 5		1	
	[B]	CHDM 10% 酸	0. 8 5	7 3	1 7 7	2 3 5	1 5	2	
実施例15	[A]	477% 酸 15% 酸	1. 1	7 2	1 5 5	2 3 0		1	
	[B]	CHDM 10% 酸	0. 8 5	7 3	1 7 7	2 3 5	1 5	2	
実施例16	[A]	477% 酸 10% 酸	1. 1	7 2	1 6 7	2 2 3		1	
	[B]	CHDM 10% 酸	0. 8 5	7 3	1 7 7	2 3 5	2 5	2	

[0095]

[Table 7]

表 7

	各層の飽和ポリエステル樹脂						[B] 7/17- 樹脂 <sup>*5</sup>  重量部	膜厚比 [A]  [B]
	組 成		固有粘度 [dl/g]	DSC				
				T <sub>g</sub> (℃)	T <sub>c</sub> (℃)	T <sub>m</sub> (℃)		
比較例 8	[A]	ホモPET <sup>*4</sup>	1. 5	73	174	240		1
	[B]	イソフタル酸 <sup>*2</sup> 10%	0. 85	73	155	229	15	2
比較例 9	[A]	イソフタル酸 <sup>*1</sup> 20%	1. 1	73	—	—		1
	[B]	イソフタル酸 10%	0. 85	73	155	229	15	2
比較例10	[A]	イソフタル酸 10%	1. 1	72	167	223		1
	[B]	イソフタル酸 20%	0. 85	73	—	—	0	2
比較例11	[A]	イソフタル酸 10%	1. 1	72	167	223		3
	[B]	イソフタル酸 10%	0. 85	73	155	229	15	1
比較例12	[A]	イソフタル酸 10%	1. 1	72	167	223		1
	[B]	イソフタル酸 10%	0. 85	73	155	229	15	10
比較例13	[A]	ホモPET <sup>*4</sup>	1. 1	73	169	252		1
	[B]	CHDM <sup>*3</sup> 10%	0. 85	73	177	235	15	2
比較例14	[A]	イソフタル酸 20%	1. 5	73	—	—		1
	[B]	CHDM 10%	0. 85	73	177	235	15	2

\* 1、\* 2、\* 3、\* 4 ; 表1と同じ意味である。

[0096] In Table 6 and Table 7, the sum totals of \*5[B] resin composition: ionomer resin and saturated polyester resin are 100 weight sections.

[Table 8]

表 8

	(i) 密着性試験	(ii) プリスター 試験	(iii) 露寧液電流試験 (mA/缶)	(iv) 試験測定結果 (露寧出量率)	(v) フレーバー 吸着	総合評価
実施例9	○	○	0.0~0.0	無	84	○
実施例10	○	○	0.0~0.2	無	28	○
実施例11	○	○	0.0~0.2	無	40	○
実施例12	○	○	0.0~0.0	無	37	○
実施例13	○	○	0.0~0.1	無	43	○
実施例14	○	○	0.0~0.0	無	82	○
実施例15	○	○	0.0~0.0	無	31	○
実施例16	○	○	0.0~0.0	無	37	○
比較例8	○	×	0.5~1.2	無	105	×
比較例9	○	△	1.2~3.6	有	170	×
比較例10	○	△	5.2~20.1	有	41	×
比較例11	○	○	2.2~8.7	無	43	×
比較例12	○	○	0.2~2.6	有	48	×
比較例13	○	×	0.4~3.2	無	101	×
比較例14	○	△	4.2~7.9	有	181	×

[Translation done.]